

(19) Japan Patent Office
(11) Patent Application

Patent Publication
S53-30996

(51) Int. Cl. 2	Identification Number	(52) Japan Classification	JPO File Number	(43) Date of Publication	March
23, 1978					
B 01 J 23/22		13(9) G 11	6703-4A		
B 01 J 23/24		13(9) G 112	6703-4A	[Number of The Inventions] 1	
B 01 J 23/70 //		13(9) G 113	6703-4A	[Examination Request] Not Yet Requested	
B 01 J 21/14		13(9) G 02	6703-4A		
B 01 J 37/00		13(9) G 01	6703-4A		(Total 9 Pages)
C 10 G 23/02		18 D 6	6974-46		

(54) Production Method of Metal-Supported Sepiolite Catalyst

(21) Patent Application Number S51-104955
(22) Date of Filing September 3, 1976
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[Professional Specification]

1. [Claims]

Production Methods of Metal-Supported Sepiolite Catalyst

2. [Claims]

[Claim-1] In preparing a catalyst for hydrotreatment of hydrocarbons using a sepiolite as the carrier material,

(a) the metal-supported process in which the sepiolite material used as is or ground, is made to contact with an aqueous solution of $\text{pH} \leq 7$ that contains one or more metal ions selected from Co, Ni, Fe, Cu, or lanthanide, making the portion of Mg in the sepiolite material to elute, and making the aforementioned metals to support;

(b) the conditioning/kneading process in which the sepiolite is kneaded with added water, making the moisture content ultimately to 20% - 350% by weight based on the dry sepiolite; and

(c) the catalyst production method by using series of processes in which the conditioned sepiolite is molded or air-dried and/or calcinated at the temperature of less than 1000 degrees C without molding.

[Claim-2] The method according to claim-1 of carrying out the preprocessing in which the sepiolite material is made to contact with an aqueous solution that contains one or more items previously selected from the groups of acids such as mineral acid, organic acid, and carbonic acid etc. ; or ammonium salts or ammonium derivative salts; and magnesium salts.

[Claim-3] The method according to claim-1 or 2 of cleaning/removing metal compounds that are simply absorbed or adhered on the surface of the sepiolite, and the aqueous solution that contains magnesium eluted from the sepiolite, after the metal-supported treatment in the metal-supported process.

[Claim-4] The method according to claim-1, 2 or 3 of adding one or more items selected from following items as an additive in the conditioning/kneading process;

- (i) Alumina hydroxide sol , alumina silica gel , silica gel or materials containing other aluminums or silicas;
- ii) bauxite, kaoline, montmorillonite, bentonite, allophane, atabalgite or other clay minerals;
- iii) higher alcohol, ester, ether, urea, amylum, sucrose, or other organic molding auxiliaries.

[Claim-5] The method according to claim-1, 2, 3, or 4 of supporting one or more metals selected from the families of Va, VIa and iron in the periodic table using a conventional method after the metal-supported process or the calcination process.

This invention is characterized by producing a catalyst obtained by supporting catalyst metals using a sepiolite as a carrier, primarily through the following three processes. They are:

- a) a process in which a sepiolite is made to contact with an aqueous solution of $\text{pH} \leq 7$ that contains one or more metal ions selected from Co, Ni, Fe, Cu, or lanthanide, making these metals supported, by the exchange of the ions between Mg in the sepiolite and these metals;
- b) a process in which the moisture content is ultimately made to 20% - 350% by weight based on the dry sepiolite by kneading with added water after the metal-supported process; and
- c) a process in which the resulting substance in (b) is molded or air-dried without molding, or/and is calcinated at the temperature of less than 1000 degrees C

A sepiolite is a porous magnesia silicate also called as meerschaum, which is produced naturally as well as synthesized using magnesium compounds and silicone compounds as the raw materials. A sepiolite has been used as a catalyst carrier for the hydrogenation of hydrocarbon gas or gasoline etc. , however it has never been used as a catalyst for the hydrogenation of heavy oils. Inventors have discovered that a catalyst obtained by using a sepiolite has unique characteristics for the hydrotreatment of heavy oils, based on which numerous suggestions have been made. This invention aims to further improve the hydrogenation activity, desulfurization activity, and the demetal activity by further improving technologies that relate to a series of catalyst productions.

The inventors have discovered that a porous magnesia silicate that differs from a sepiolite material physically and chemically, can be obtained by molding a sepiolite at high moisture content after the grinding or kneading of the sepiolite.

Furthermore, the inventors have also proved that a catalyst with a high activity greater than the activity when a conventional support method is used, can be obtained by making a sepiolite to support catalyst metals utilizing the ion exchangeability.

Thereafter, the method of this invention was obtained as the result of extensive studies while taking notice in that the influences on various performances such as the catalyst property, activity, selectivity, and the life span of the obtained catalyst can largely be differ depending on the production processes such as a metal-supported method, carrier preprocessing method, and a molding method with sepiolite catalysts.

When so called catalyst metals such as Co, Ni etc. , is supported to a sepiolite utilizing its ion exchangeability, although the cause is not verified (more than likely, due to the loss of the electrostatic intermolecular force etc.), the pore volume of a sepiolite and the phenomenon of specific surface area have been observed. For the reason, in spite of the activity of supporting catalyst metals becoming greater comparing to when a conventional carrier is used, the metal-supported catalyst obtained by an ion exchange method using a sepiolite as is or the ground substance as a carrier has not yet provided sufficient performances as a catalyst for the hydrotreatment of hydrocarbons.

However, on the other hand, a sepiolite has extremely unique characteristics of recovering the pore volume and

specific surface area that have been decreased in the process of the ion exchange by molding it after adjusting the moisture content through the process of kneading with added water or simple kneading, and furthermore, even greater pore volume and specific surface area may be obtained depending upon the selection of conditions. This is due to the characteristics of a sepiolite, differing from other minerals, that a sepiolite can still be molded into desired shapes even when it contains a large volume of water. For the moisture content, a sepiolite can be made to contain 20% - 350% by weight based on the dry weight. This is characterized in that the greater the moisture content is, the greater the pore volume and specific surface area of the molded or dried as is or calcinated substance obtained becomes, and that, to more advantages, the pore distribution becomes sharper and the breaking strength also become greater.

Thus, the sepiolite catalyst caused the unexpected multiplier effect based on the combinations of metal-supported method by new ion exchange method and the kneading/conditioning and the molding processes, and very significant increase in the catalyst life span and a catalyst activity as well as improvement in physical characteristics have come to a recognition.

With the catalyst relates to this invention, in the heavy oil hydrotreatment, a high demetal activity is maintained and the activities for desulfurization and denitrogen are significantly increased, and even in the light oil hydrotreatment, the significant increase in a desulfurization activity, a denitrogen activity and a hydrogenated activity come to a recognition. Therefore, the method of this invention is characterized by obtaining an affordable, long life, and highly active catalyst that can be used for every hydrotreatment for light oils as well as heavy oils.

The raw material sepiolite can be either a naturally occurring mineral or a synthesized substance. A naturally occurring sepiolite normally contains a large amount of moisture, however since it will be treated with an aqueous solution, there is no need for previously removing the moisture. The grain size of a raw material is not particularly restricted and is to be adjusted by grinding and ridding as required depending upon the conditions in the kneading or molding method. The desirable riddling size is normally less than 50-mesh. The method of grinding can be a conventional method of either dry or wet method. Also, according to researches by inventors, it is proven that treating a sepiolite at a high temperature prior to the metal-supported process causes a negative influence in obtaining a high desulfurization activity catalyst, and therefore it is desirable to use a sepiolite either without any heat treatment or with a low moisture treatment when some heat treatment is required.

To support a catalyst metal to a sepiolite, firstly an aqueous solution is prepared using one or more metal chlorides selected from Co, Ni, Fe, Cu, lanthanide, or mineral acid salts such as sulphate and phosphate etc. , or organic acid salts such as oxalate, acetate, tartrate etc. , or other water soluble salts such as double salt, complex salt etc. , then the solution is contacted with a sepiolite to support these metals by exchanging the ions with magnesium in the sepiolite.

An aqueous solution is normally used within the range of $\text{pH} \leq 7$. The solution may be used with pH less than 1, in which case, however, it is necessary to particularly take notice in that the magnesium in a sepiolite elutes excessively, causing the sepiolite structure to be destroyed.

An aqueous solution of metal compounds may be used as is, or (1) mineral acids such as nitric acid, sulfuric acid, hydrochloric acid, and phosphoric etc. ; or organic acids such as formic acid, and acetic acid etc. ; or (2) ammonium salts for these metals or nonmetal organic acid salts; or (3) magnesium salts etc. may be added.

One or more of these additives may be mixed.

The types and percentages of additives are determined in accordance with the types of support metals, support ratios, and the characteristics of a sepiolite material or the intended use of an obtained catalyst.

For supporting more than 2 types of metals, normally more than 2 types of aqueous solutions containing the ions of such metals are used, however, a separate solution may be used for each metal so that the support may be carried out individually.

The metal maximum support ratio in the aforementioned process is a measure of approximately 3% - 4% by weight as a metal oxide, regardless of the types or concentrations of additives or types of support metals. The amount of magnesium eluted by the ion exchange with metals virtually responds to the amount of the metals, therefore the greater the metal support ratio is, the dissolution rate of magnesium become greater.

Although under the very restricted condition, the mole ratio between the amount of these support metals and the amount of the dissolved magnesium may become 1.0, normally the dissolved molar quantity of magnesium is greater than the molar quantity of support metals. Particularly, if the pH of an aqueous acid is smaller, when a high temperature treatment is applied, when the contacting time is long, or when a sepiolite material is used untreated, this aptitude

is more evident. According to inventors' knowledge, even when the metal ion concentration of an aqueous acid is extremely low, it is possible to support metals up to the maximum support ratio of a sepiolite.

These phenomenon cannot be observed at all in any conventional metal-supported methods, for example dip method or absorption method.

Thus the sepiolite that metal-supported Co, Ni etc. has a high activity as is, however, this invention aims at producing a catalyst for a wide range of hydrotreatment of hydrocarbons by further kneading, conditioning, molding, and calcinating this metal-supported sepiolite.

The kneading process is carried out by adding a sufficient amount of water, however the amount of water may be arbitrarily selected according to the characteristics of the sepiolite material, desired various characteristics or performances of catalyst, and the kneading conditions. Normally, the amount of water suitable for the conditioning after the kneading process, is added in numbers during the kneading process. Also, the kneading is normally carried out by using a conventional kneading machine, a steam-kneading machine or a molding machine such as extruder etc. , however it can also be carried out by any other methods provided that it brings the same effect. Generally the pore volume and specific surface area of a sepiolite are increased by carrying out the kneading process.

Since it has been experimentally proven that the increased pore volume etc. vanishes if treatments such as metal-support etc. were carried out in the aqueous solution after the kneading process, it is not appropriate to carry out a metal-supported treatment after the kneading process. It is presumed that this is due to the loss of the

electrostatic actions that exist among sepiolite particles, or among sepiolite fibers. The kneaded substance is then molded when the moisture content is ultimately adjusted to 20% - 350% by weight based on the dry sepiolite.

The moisture content has a considerable influence on the characteristics of the obtained substance as well as the level of difficulty in the molding process. Consequently, the moisture content is determined based on the considerations on the characteristics of a sepiolite material, after-mentioned types and the amounts of additives, the characteristics of kneaded substance, the molding method, and furthermore, the intended use etc. of the obtained catalyst. Normally the moisture content is conditioned to 20% - 350% by weight based on a sepiolite in the absolute condition, however 50% - 280% by weight is preferred. When the moisture content was made less than 20%, that desired catalyst property such as pore volume cannot be achieved and a molding by a conventional molding method become difficult. Also, if the moisture content is conditioned to more than 350%, a sufficient breaking strength of catalyst cannot be achieved and thus it is considered impractical. If additives are concomitantly used, aforementioned moisture content may be applied to the total amount including the additives.

After the kneading/conditioning process, the resulting substance is either air-dried or/and calcinated at the temperature of 1000 degrees C. This process may be carried out with the conditioned substance as is, in other words, in the aggregated condition, or in the molded condition using a conventional molding method such as a tableting machine or an extrusion molding machine. The aggregated substance is then ground down to a predetermined grain size after the air-dry calcination process, allowing it to be used in the slurry condition. The shape and size of catalyst is determined according to the intended use and/or the

method. The production method is also selected so that the breaking strength of catalyst is adequate for the use conditions and the air-dry and calcination temperatures may also be determined as required.

A series of processes in producing a catalyst for hydrotreatment using a sepiolite as the carrier material has been described above, however, if required, according to the researches by inventors, appropriate catalysts for various purposes can be obtained by incorporating additional processes described below.

Small amount of impurities such as calcium carbonate, magnesium carbonate, or magnesium calcium carbonate may be contained in a commonly used sepiolite. Although a part of these impurities is removed in the metal-supported process that uses an aqueous acids, the remaining impurities may have a negative effect on the activity of the obtained catalyst, particularly on the hydrogenation activities such as desulfurization and deacidification. Also, since these impurities are dissolved in the metal-supported process, the breaking strength of catalyst can be reduced.

Furthermore, the dissolution of these impurities makes the collection of a waste solution from the metal-supported process more difficult.

A preprocessing process is carried out to address such drawbacks.

For the preprocessing, an aqueous solution that contains one or more substances selected from magnesium salts, mineral acid, organic acid, carbonic acid, ammonium salt, ammonium derivative salt is used.

Mineral acids used here can mean nitric acid, sulfuric acid, hydrochloric acid, phosphoric etc. , and organic acids can mean formic acid, formic acid, acetic acid, tartar etc. Also for a carbonic acid, an aqueous solution of a carbonic acid gas dissolved in water under the normal pressure or a pressurized condition is normally used. Furthermore, for ammonium salt, ammonium nitrate, ammonium sulfate, ammonium phosphide, ammonium carbonate, ammonium oxalate, ammonium acetate, ammonium tartrate etc. are used; and for ammonium derivative salts, for example, trimethylamine hydrochloride, aniline hydrochloride is used.

The composition and temperature of these processing solutions may be arbitrarily selected, however it is effective to use them in the pH range of between 1 - 7. Even if a solution is a strong acid of pH less than 1, the solution may be used providing that the treatment is done in a short period of time.

In the preprocessing, there are no particular restrictions on either the processing temperature or on the processing time, and the processing is normally carried out at the temperature of less than 100 degrees C and in more than several minutes. Depending on the characteristics of a sepiolite, a short time processing may sufficiently achieve the desired purpose.

Naturally, the elution of magnesium is observed in the processing solution, and this eluted amount of magnesium can vary depending on the processing conditions of a sepiolite. Normally the amount of elution become greater when the pH of the processing solution is lower and the processing time at a high temperature is longer.

Inventors have checked the amount of magnesium in a sepiolite before and after the preprocessing to confirm that the amount of magnesium eluted is attributed to the

impurities such as magnesium hydrate, magnesium carbonate and a dolomite component in the sepiolite, and therefore come to a recognition that one of the major reasons why the preprocessing contributes to a positive effect on the metal-supported process was in the elution of the majority impurities.

The sepiolite after the preprocessing is used as is or cleaned by water again then used.

Also, primarily for the purpose of increasing the breaking strength of obtained catalyst, one of the following is added as an additive:

- i) Alumina hydroxide sol, alumina silica sol, silica sol or materials containing other aluminums or silicas;
- ii) bauxite, kaoline, montmorillonite, bentonite, allophane, atabalgite or other clay minerals;
- iii) higher alcohol, ester, ether, urea, amylum, sucrose, or other organic molding auxiliaries.

These additives are sometimes added as the filler besides increasing the breaking strength. Also, by selecting other catalyst production conditions, these additives may have an effect on the property and activity of a catalyst, depending on the additives. In aforementioned compounds in (i) group, these additives have an effect to provide a sepiolite the thermal stability, and also compounds in (iii) group have an effect of making the kneading and molding processes smoother.

For the amount of additives for these purposes, in (i) group compounds, 0.5% - 90% by weight, preferably 1% - 80% by weight, more preferably 1% - 20% by weight, as an oxide anhydride is added, and in (iii) group compounds, 1% - 30%

by weight is added. Therefore, the types and the amounts of additives can be arbitrarily determined based on the consideration for the intended use etc. of catalyst. For example, these additives may also be used on a sepiolite excessively. Selecting and combining additives from (i) (ii) (iii) groups may further enhance various effects as well. Normally, these additives are finely ground or sludged in the kneading process prior to the addition, however they can be mixed before supporting metals such as Co, Ni etc.

Besides the aforementioned additives, water soluble mineral acids, organic acids, or metal acids or compounds used in the preprocessing process such as ammonium salts, ammonium derivative salts, or magnesium salts etc. of these acids may be added, however if these components remain in the sepiolite, these additives are not required.

The activity of catalyst produced by the method in this invention is high for hydrotreatment of heavy oils and is effective as a catalyst with an excellent reaction selectivity, however, it further supports one or more catalyst metals selected from the families of Va, VIa and iron in the periodic table according to the intended use. V as a Va family, Cr, Mo, and W as a VIa family, and Co, Ni, Fe etc. are as an iron family are respectively used. A support may be carried out after metal supporting Co and Ni etc. , as is or immediately after the cleaning, however normally the molded substance is air-dried or calcinated at the temperature less than 1000 degrees C, and then the resulting substance is supported. For these metal support, the metal compounds are dissolved into an aqueous solution and then the support may be carried out with a conventional method such as dipping or spraying method etc. For example, a basic aqueous solution that contains para-ammonium molybdate, para-ammonium tungstate, sodium silicotungstate, etc. or aqueous acids such as vanadium

oxide, vanadium oxalate etc. is used. The types of metals supported or the support amount is determined according to the intended use etc. of a catalyst.

The support amount is normally 0. 1 - 30% by weight, preferably 0. 5 - 20% by weight as a metal oxide. With a catalyst for hydrotreatment using a conventional alumina or alumina silica as the carrier, although it is known that the activity become greater as the support amount of these metal increase, with a catalyst relates to this invention, however, a high activity can be achieved using a small amount of supporting metal, and furthermore, the effect does not change even if the support amount increases.

As described earlier, although the catalyst obtained by the method of this invention is extremely affordable, a catalyst with a high activity, a high selectivity rate, or a long life span can be produced according to the characteristics of target hydrocarbons, the purpose of hydrotreatment, or reaction conditions etc. by the appropriate selections or combinations. Consequently, the types of hydrotreatment and the types of target hydrocarbons using a catalyst obtained by the method of this invention is extremely wide ranging. In other words, a catalyst obtained by this invention is effective for the desulfurization, denitrogen, and the hydrogenated reaction of light oils such as gasoline, kerosene etc. and also effective for reactions such as the demetal, deasphaltene, desulfurization, denitrogen, hydrogenation, and the hydrogenation degradation of heavy oils such as subatmospheric bottom oil, oil sand, and bitumen, etc.

Since the catalyst obtained by this invention is effective for a variety of hydrotreatments of extremely large variety of hydrocarbons, the reaction conditions in this invention are also wide ranging. However, the hydrogen partial pressure is normally at 10 - 350 barometric pressure,

preferably 15 - 300 barometric pressure, and the reaction temperature is in the range of normally at 200 degrees C - 470 degrees C, preferably 200 degrees C - 450 degrees C. These reaction conditions are arbitrarily selected according to the characteristics of hydrocarbons, the purpose of hydrotreatment, and the reaction methods etc. Similarly, the reaction method in this invention method can be the one of publicly known methods, for example, a conventional distribution fixed bed, a moving bed, or a fluid bed system is used.

Following is the explanation of samples for the purpose of explaining this invention in more details. Unless otherwise mentioned particularly, all "portion" and "%" are based on by weight.

Example-1

The coarse ground (4mm - 5mm in diameter) of a sepiolite material produced in Korea was used. This coarse ground substance was dipped in the aqueous solution that contains 0.1 molar/l of nickel nitrate for 2 days and nights, and then was cleaned thoroughly with warm water at the temperature of 50 degrees C. Obtained nickel supported sepiolite was then calcinated at the temperature of 500 degrees C for 2 hours. Upon the analysis of the resulting substance, 2.1% of nickel oxide was found. Upon the analysis of the nickel dip solution, magnesium dissolved in the solution in the amount of 2.6 times (in atomic ratio) of the nickel supported to a sepiolite.

Then, approximately 3 portions of water was added to the 1 portion of this nickel-supported sepiolite, both of which were thoroughly kneaded together using a kneading machine. In this kneading process, the sepiolite was kneaded and at the same time aggregated mineral ores were ground and pulverized. After thorough kneading ready for molding, the

kneaded substance was dried at 60 degrees C for a short period of time, then water was added to condition the substance making the moisture content at approximately 130%. After the conditioned substance was kneaded for a short period of time while ensuring to maintain the moisture content, the resulting substance was molded into a tubular shape of 1.7mm in diameter. The molded substance was air-dried for 5 days in the atmosphere, then it was calcinated at the temperature of 500 degrees C for 1 hour to obtain the nickel supported sepiolite catalyst. The physical characteristics of this catalyst and a sepiolite material calcinated at the temperature of 500 degrees C for 1 hour are shown in Table-1.

Table-1

Characteristics	Nickel Supported Sepiolite (500 degrees C calcination)	A Sepiolite Material (500 degrees C calcination)
Specific Surface Area (BET method)	232m ² /g	153
Specific Surface Area (mercurial injection method >30 Angstrom)	133m ² /g	65
Pore Volume (mercurial injection method >30 Angstrom)	0. 68cc/g	0. 52
Pore Distribution (mercurial injection method >30 Angstrom)	0. 19cc	0. 12
30 - 200 Angstrom	0. 44cc	0. 20
200 - 600 Angstrom	0. 05cc	0. 18
600 Angstrom or more		
Breaking Strength (radial)	3. 5 - 5. 0Kg	-

According to Table-1, it is evident that the physical characteristics of the nickel supported sepiolite molded

catalyst obtained by the method of this invention is largely differ from the characteristics of the sepiolite material. In other words, the molded substance compared to the sepiolite material has: (1) a larger specific surface area, (2) a larger pore volume, and (3) a sharper pore distribution. Based on the above, the nickel supported sepiolite molded substance by the method of this invention has clearly different characteristics from the substance obtained by simply supporting a nickel to a sepiolite material and it is presumed that the treatment process of a sepiolite in this invention is different from mere molding process.

Then hydrotreatment of the degradation oil consisting of 2. 4% sulfur, 14ppm vanadium, and the bromine number 26 (boiling point 200 degrees C - 500 degrees C) was carried out using this catalyst. The reaction using a conventional circulating reaction device with the reaction temperature at 350 degrees C, hydrogen partial pressure at 50%, and the fluid ambience rate at 1. 0Hr-1 was carried out. Upon the analysis of the generated oil after 50 hours, it was observed that the sulfur was down to 2. 1%, vanadium was down to 5 ppm and the bromine number was also down to 16.

Example-2

The nickel supported sepiolite molded substance obtained in Example-1 was air-dried and then calcinated at 200 degrees C for 1 hour. The resulting substance was dipped into an ammoniacal solution of para-ammonium molybdate and calcinated at 500 degrees C for 1 hour to obtain a nickel and molybdenum supported sepiolite catalyst. Upon the analysis of this catalyst, 2. 0% of NiO and 4% of MoO₃ was found. Upon measuring the physical characteristics using the same method as Example-1, other than a slight decrease in the specific surface area (BET method) down to 22. 6m²/g, and the pore volume down to 0. 66cc/g, the measuring result

was similar to the characteristics of the nickel-supported catalyst obtained in Example-1.

Using this catalyst, the same concentric device as in Example-1, and under the same reaction conditions, hydrotreatment of the same degradation oil was carried out. Upon the analysis of the generated oil after 50 hours, it was observed that the sulfur was down to 0.89%, vanadium was down to 3 ppm and the bromine number was also down to 14.

Example-3

In the kneading process of non-molded nickel supported sepiolite in Example-1, predetermined amount of para-ammonium tungstate was added to prepare the nickel, tungsten supported catalyst. The kneading process, conditioning process, molding process and the calcination process were carried out in nearly same method and conditions as Example-1. Upon the analysis of the obtained catalyst, 2.0% of NiO and 7.8% of WO₃ was found. Also the physical characteristics of the catalyst was, same as in Example-2, virtually similar to the catalyst obtained in Example-1.

Using this catalyst, same reaction device as Example-1, hydrotreatment of an atmospheric bottom oil that contains 2.62% of sulfur, 3.600ppm of nitrogen, 3.2% of n-heptane insoluble, 130ppm of vanadium, 34ppm of nickel was carried out. The reaction was carried out with the reaction hydrogen pressure at 140 MPa, reaction temperature at 420 degrees C, and the fluid ambience rate at 0.5Hr⁻¹, and after 50 hours, the generated oil was analyzed to obtain following results. sulfur: 0.31%, nitrogen: 2100ppm, n-heptane insoluble: 0.3%, vanadium \leq 2ppm, nickel 13ppm.

Example-4

Copper, molybdenum supported sepiolite catalyst was prepared in the same way as Example-1.

For a sepiolite material, a Spanish product coarse ground to 1 - 2mm was chosen, which was dipped into an aqueous solution that contains 0. 1molar /l of magnesium nitrate for 1 day and night, then the resulting substance was cleaned thoroughly with warm water before it was used.

Then the resulting substance was dipped into an aqueous solution that contains 0. 02molar /l of copper nitrate for 5 hours, and then cleaned with warm water, and then cleaned again with 5% ammonia water, then was dried at 120 degrees C for 2 hours. Then the resulting dry substance was wet ground for 10 hours together with aluminum hydroxide sol that contains 16% of alumina in the amount of 3% of absolute alumina equivalent, 25% of U. S. atabalgite clay, and 200% of water. Then the resulting substance was kneaded thoroughly together with the added ammoniacal solution of para-ammonium molybdate, then the conditioning was carried out by repeating the cycles of drying (at 60 degrees C) and water spraying so that the moisture content would reach at 210%. After the conditioned substance was molded into a tubular shape of 1. 7mm in diameter, it was air-dried for approximately one week, then was calcinated at 500 degrees C for 2 hours to obtain the copper, molybdenum supported catalyst. Upon the analysis of this catalyst, 2. 4% of CuO, 6. 4% of MoO₃ was found. Upon the measuring physical characteristics of the substance in the same method as Example-1, following values were obtained.

Table-2 Characteristics of Copper, Molybdenum Supported Catalyst

Specific Surface Area (BET method)	210m ² /g
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Specific Surface Area (mercurial injection method > 30 Angstrom)	107m ² /g
Pore Volume (mercurial injection method > 30 Angstrom)	0. 74cc/g
Pore Distribution (mercurial injection method >30 Angstrom)	
30 - 200 Angstrom	0. 13cc/g
200 - 600 Angstrom	0. 35cc/g
> 600 Angstrom	0. 26cc/g
Breaking Strength (radial)	2. 2 - 4. 7Kg

The hydrotreatment of the same oil using this catalyst and the same device under the same reaction conditions as Example-3 was carried out. Upon the analysis of the generated oil, following result was obtained.

sulfur; 0. 28%, nitrogen; 2200ppm, vanadium \leq 2ppm, and nickel \leq 2ppm.

Example-5

Cerium, molybdenum supported sepiolite catalyst was prepared in the same way as Example-4. However cerium supported sepiolite was obtained by dipping coarse ground Spanish sepiolite into an aqueous solution that contains 0. 0lmolar /l of nitric acid and 0. 1molar /l of magnesium nitrate, stirring for 5 hours, then dipping the resulting substance into an aqueous solution that contains 0. 1molar /l of cerium nitrate for 5 hours. After this cerium supported sepiolite was cleaned thoroughly with warm water, the resulting substance was then wet ground for approximately 10 hours together with aluminum hydroxide sol that contains 16% of alumina to a sepiolite in the amount of 5% of absolute alumina equivalent, 25% of bauxite that contains 5. 1% of Fe₂O₃, 1. 8% of TiO₂, and 150% of water, based on 120 degrees C dry substance standard. Then this ground substance was kneaded thoroughly together with

added ammoniacal solution of para-ammonium molybdate, then the conditioning was carried out so that the moisture content would reach at 125%. After this was molded into a tubular shape of 1.0mm in diameter, it was air-dried for approximately one week, then the resulting substance was calcinated at 650 degrees C for 2 hours to obtain cerium, molybdenum supported catalyst. Upon the analysis of this catalyst, 1.2% of Ce_2O_3 , 3.1% of MoO_2 was found. Upon the measuring physical characteristics of the substance, the specific surface area (mercurial injection method, dia. ≤ 30 angstrom) was $146m^2/g$ and the pore volume was $0.57cc/g$.

The hydrotreatment of the same oil using this catalyst and the same device under the same reaction conditions as in Example-3 was carried out. The characteristics of the generated oil after 50 hours of reaction was as follows. sulfur ; 0.45%, vanadium $\leq 2ppm$.

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